

Giant electrooptic response of excitons in porphyrin J-aggregates

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Abstract

J-aggregates of tetraphenyl porphyrin tetrasulfonic acid (TPPS) doped in a polyvinylalcohol (PVA) thin film were studied by highly sensitive electroabsorption spectroscopy using a multichannel lock-in amplifier. A change in the static polarizability $\Delta\alpha$ of the aggregate upon electronic excitation was determined as 20000–39000 Å³, from which the size of coherent delocalization of excitons was evaluated to be 60–80 molecules. This is 10 times larger than that previously reported. At least one of the reasons of the difference is found to be the content of water molecules in the polymer matrix.

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1. Introduction

J-aggregates are self-assembled molecular systems of dyes, and they show strong, sharp red-shifted absorption band, called the J-band, from that of the monomer [1,2]. Porphyrin J-aggregates are of special interest, since they are model substances for aggregates of the light-harvesting antenna chlorophyll with a ‘storage-ring’ configuration and of primary charge-separation systems in photosynthesis [3]. A model of identical molecules aligned one-dimensionally has been proposed to explain the electronic spectrum of the J-aggregate. The J-band has been assigned to a Frenkel exciton [4–6], where intermolecular interaction between transition dipole moments results in the coherent delocalization of excitons over an aggregate.

It is known that J-aggregates have a hierarchical structure that consists of the small-size coherent aggregates and large-scale rod-shaped aggregates. The former is a meso-aggregate, characterized by delocalized exciton, while the latter is a macro-aggregate composed of a large number of meso-aggregates, whose sizes depend on the method of preparation [7]. Spectroscopic aggrega-

tion number is the size of a meso-aggregate, i.e., the coherent aggregation number N_c .

Electroabsorption (EA) spectroscopy is a sensitive method to probe the detailed structure of electronic excited states of aggregates and monomers, i.e., the static polarizability and the static dipole moment. However, presently available experimental results are rather scattered to evade a simple theoretical explanation as follows (see also Table 2). A large change in the static polarizability $\Delta\alpha$ of J-aggregates of pseudoisocyanine (PIC) was reported by Misawa and Kobayashi [8]. The N_c was evaluated to be 80–120 using a scaling law, where the ratio of $\Delta\alpha$ of the aggregate to that of the monomer is a direct measure of N_c [8,9]. The N_c of porphyrin (TPPS) J-aggregates was also evaluated in the same series of the experiment, but it was reported to be as small as 4–6 [10,11]. The EA signals of size-controlled J-aggregates of DNA-templated cyanine dyes, DiSC(5), were analyzed with the scaling law [12,13]. They concluded that $N_c = 4–6$ for J-aggregates while $N_c = 2$ for H-aggregates, and $\Delta\alpha$ was shown to have a different size dependence between J- and H-aggregates.

The variation in N_c was attributed to different configurations of aggregates, but there is also a report, in which the straightforward scaling law is questioned and mixing of charge-transfer nature into the Frenkel

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exciton is proposed to be more important [14]. In addition, a large change in the static dipole moment $\Delta\mu$ was observed for PIC J-aggregates [8], though $\Delta\mu$ of the aggregate was expected to be no more than that of the monomer [9,15]. Thus, the electric field effects on J-aggregates need further systematic studies.

In the present Letter, we have reinvestigated the effects of external electric field on the absorption spectra of the J-aggregates and monomer of TPPS using a multichannel lock-in amplifier for signal detection [16], by which a larger $\Delta\alpha$ than that in the previous report has been observed for the J-aggregates.

2. Experimental

Tetraphenyl porphyrin tetrasulfonic acid (TPPS, reagent grade, Tokyo Kasei Kogyo) was used without further purification. Polyvinylalcohol (PVA, Kanto Kagaku) was used as a host matrix in a film form. A suitable amount of TPPS (8 mg for J-aggregate-sample or 2 mg for monomer-sample) and 80 mg PVA were dissolved in 2 cm³ distilled water, and the solution was coated on glass substrates by a spin coating method. The thickness of the film samples was ≈ 0.5 μm (J-aggregate-sample) or ≈ 1.0 μm (monomer-sample). For EA spectroscopy, a pair of aluminum electrodes with a gap separation of 0.4–0.5 mm was deposited on glass substrates by vacuum evaporation. The gap separation was measured for every sample with a microscope.

White light from a xenon-lamp (Hamamatsu, L2273) was focused inside of the gap. An ac electric field ($F_{\text{ext}} = F_0 \sin(2\pi ft)$): $F_0 \approx 10^6$ V/m and $f = 235$ – 2035 Hz) was applied between the electrodes by using a function generator (Iwatsu, SG-4105) combined with a high-voltage amplifier (Matsusada, HEOPT-5B20) to detect the field-induced absorbance change through a spectrometer with a multichannel lock-in amplifier [16]. Since the multichannel lock-in amplifier has 128 detection channels connected to 128 avalanche photodiodes, all wavelength regions of interest were detected simultaneously, reducing a measurement time by two orders of magnitude, or improving the signal-to-noise ratio by one order of magnitude for the same measurement time. The absorbance changes due to the Pockels and Kerr effects were detected at the modulation frequency f and its second harmonic $2f$, respectively.

The absorption spectra of the samples were measured using a spectrophotometer (Shimadzu, UV-3101PC). In order to determine the Stark parameters accurately, the absorption was measured at the same spot as in the EA measurement. Otherwise, absorption inhomogeneity of the sample may introduce sizable errors.

The absorption spectra and Stark-modulation spectra due to the Pockels and Kerr effects, shown in Fig. 1, are characterized by a relatively weak Q-

band in the visible region and a strong B-band in the near-ultraviolet. Note that the aggregate shows a larger Kerr signal than for the monomer by two-orders of magnitude and that both aggregate and monomer show a Pockels signal.

3. Method of data analysis

The EA signals were analyzed with the Liptay equation [17] adjusted to rod-shaped aggregates dispersed in a 2-dimensional (2-D) plane and to plane-shaped monomers dispersed in a 3-D space as follows.

When an electric field \mathbf{F} is applied, molecules have changes in the dipole moment $\Delta\mu$ and in the static polarizability $\Delta\alpha$ between the ground and excited states upon electronic excitation. Since TPPS molecules were fixed in the polymer matrix and the absorbance change corresponding to the zeroth-order derivatives of the linear absorption spectrum did not appear in this experiment, the orientation effect and the change of transition dipole moments due to the applied electric field can be ignored. On this condition, the absorbance change (ΔA) is given by [17,18]

$$\Delta A = \left\langle (\Delta\mu \cdot \mathbf{F}) \frac{v}{h} \frac{\partial(A/v)}{\partial v} + \frac{1}{2} (\mathbf{F} : \Delta\alpha : \mathbf{F}) \frac{v}{h} \frac{\partial(A/v)}{\partial v} + \frac{1}{2} (\Delta\mu \cdot \mathbf{F})^2 \frac{v}{h^2} \frac{\partial^2(A/v)}{\partial v^2} \right\rangle. \quad (1)$$

Here, v is the probe-light frequency. Averages of $\Delta\mu$ and $\Delta\alpha$ over the angular distribution of molecular orientations are represented by the bracket, $\langle \rangle$. Since absorption bands of TPPS (Q- and B-band) are sharp, $v\partial(A/v)/\partial v$ can be reduced to $\partial A/\partial v$.

When the probe light is not linearly polarized and sample molecules are dispersed isotropically, Eq. (1) is expressed by

$$\Delta A = \left\{ \frac{1}{20} (3\text{Tr}\Delta\alpha + \Delta\alpha_m) \frac{\partial A}{\partial E} + \frac{1}{5} |\Delta\mu|_{2f}^2 \frac{\partial^2 A}{\partial E^2} \right\} |\mathbf{F}|^2, \quad (2)$$

where $\Delta\alpha_m$ is the change in the static polarizability with respect to the direction of the transition dipole moment. Since films prepared by spin coating are ≈ 0.5 μm thick for J-aggregate samples and the macro-aggregate size is reported to be ≈ 1.0 μm [19,20], J-aggregate rods should be oriented on the film plane. In this case, there should be no Stark effect for the applied electric field vector perpendicular to the film plane. On the other hand, for the electric field vector parallel to the film plane as adopted in the present experimental setup, Eq. (1) is expressed by

$$\Delta A = \left\{ \frac{1}{8} (\text{Tr}\Delta\alpha + \Delta\alpha_m) \frac{\partial A}{\partial E} + \frac{1}{4} |\Delta\mu|_{2f}^2 \frac{\partial^2 A}{\partial E^2} \right\} |\mathbf{F}|^2. \quad (3)$$

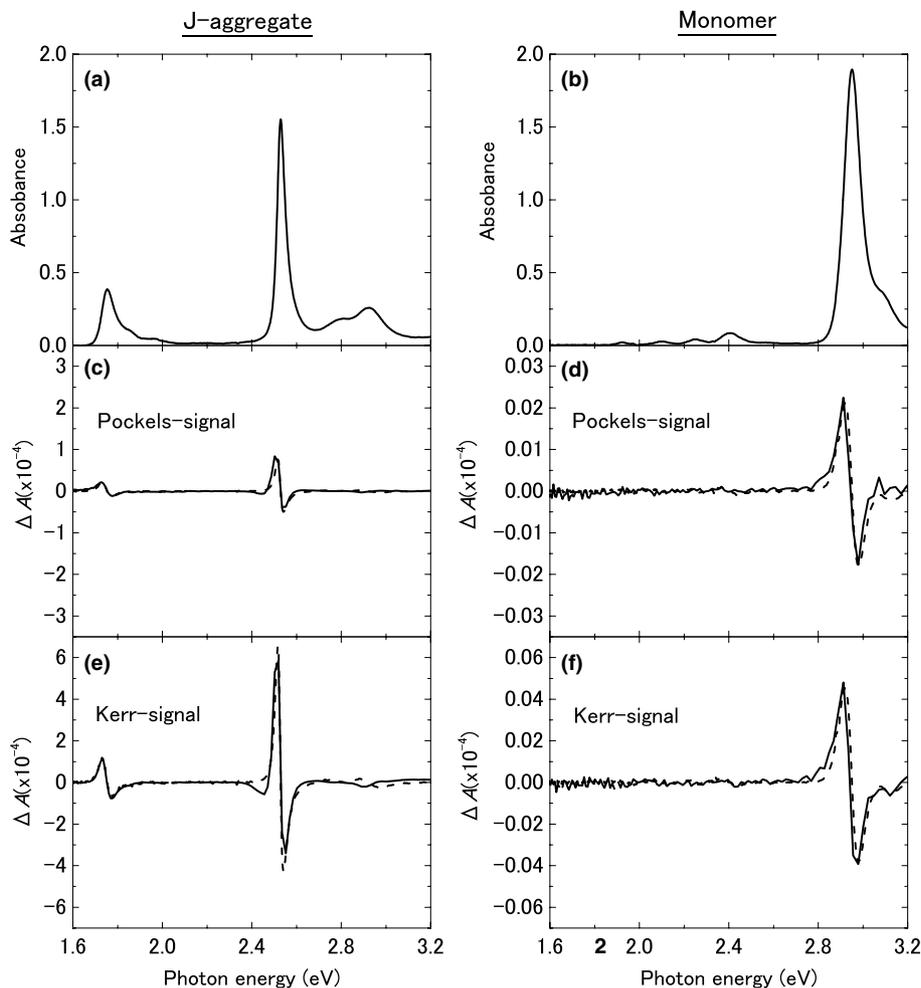


Fig. 1. Absorption spectra of J-aggregate (a) and monomer (b) of TPPS. Solid curves are Stark spectra due to the Pockels effect and broken curves are fitting curves by the first-derivative of the linear absorption spectra of J-aggregate (c) and monomer (d) of TPPS, respectively. Solid curves are Stark spectra due to the Kerr effect and broken curves are fitting curves by the sum of second- and first-derivatives of the linear absorption spectra for J-aggregate (e) and monomer (f). Electroabsorption data (c)–(f) are taken with the following parameters. Electrode-gap: 0.35 mm, voltage: 1100 V, frequency: 235 Hz, measurement time: 1 h.

In Eqs. (2) and (3), the Pockels effect does not contribute to the absorption change, because the ensemble sum of $\Delta\mu$ in isotropic systems disappears by cancellation.

When the sample molecules are oriented in the direction of the applied electric field, Eq. (1) can be rewritten as

$$\Delta A = \left\{ |\Delta\mu|_f \frac{\partial A}{\partial E} \right\} |\mathbf{F}| + \left\{ \frac{1}{2} \Delta\alpha \frac{\partial A}{\partial E} + \frac{1}{2} |\Delta\mu|_{2f}^2 \frac{\partial^2 A}{\partial E^2} \right\} |\mathbf{F}|^2. \quad (4)$$

Since the absorption change due to the Pockels effect appeared in this study, the sample molecules were oriented to some extent. In this case, the absorption change can be written as

$$\Delta A = \left\{ A_0 |\Delta\mu|_f \frac{\partial A}{\partial E} \right\} |\mathbf{F}| + \left\{ B_0 \Delta\alpha \frac{\partial A}{\partial E} + C_0 |\Delta\mu|_{2f}^2 \frac{\partial^2 A}{\partial E^2} \right\} |\mathbf{F}|^2, \quad (5)$$

where A_0 , B_0 , and C_0 are determined by the degree of molecular orientation, which can be determined by comparing $|\Delta\mu|_f = |\sum \Delta\mu_i|/N$ determined from the Pockels effect with $|\Delta\mu|_{2f} = \sqrt{\sum |\Delta\mu_i|^2}/N$ from the Kerr effect, with N being the number of monomers or J-aggregate.

Since J-aggregate has a 1-D structure and TPPS monomer has a planar structure, it is assumed that the static polarizability change tensors of J-aggregate $\Delta\alpha_{\text{agg}}$ and monomer $\Delta\alpha_{\text{mon}}$ (its transition dipole moment is in the direction of the z -axis) are

$$\Delta\alpha_{\text{agg}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \Delta\alpha \end{pmatrix} \quad \text{and} \quad \Delta\alpha_{\text{mon}} = \begin{pmatrix} \Delta\alpha & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \Delta\alpha \end{pmatrix}. \quad (6)$$

The local field \mathbf{F} has to be corrected by the Lorentz field

Table 1
Stark parameters of the TPPS J-aggregate and monomer

Absorption band	$ \Delta\mu _f$ (Debye) ^a	$ \Delta\mu _{2f}$ (Debye) ^b	$\Delta\alpha$ (Å ³) ^b
<i>J-aggregate</i>			
B-band (2.54 eV)	0.06–0.6	<10	20000–39000
Q-band (1.76 eV)	0.08–0.8	<10	20000–39000
<i>Monomer</i>			
B-band (2.96 eV)	0–0.03	<1	340–490
Q-band (2.40–1.93 eV)	<0.03	<2	300–400

^a $|\Delta\mu|_f$ determined by the modulation spectra due to the Pockels effect using Eq. (4). The values are widely distributed from sample to sample.

^b $|\Delta\mu|_{2f}$ and $\Delta\alpha$ determined by the modulation spectra due to the Kerr effect using Eq. (5). Averages of three sample values are shown. For each sample the largest value for $C_0|\Delta\mu|_{2f}^2$ is estimated and C_0 is assumed to be 1/5 for monomer and 1/4 for aggregate to get the largest estimate for $|\Delta\mu|_{2f}$. For $\Delta\alpha$, B_0 is taken to range from 7/20 to 1/2 for monomer and from 1/4 to 1/2 for aggregate.

Table 2
The coherence aggregation number of J-aggregates

Author	Year	Aggregation number	Measurement
<i>Porphyrin (TPPS)</i>			
Ohno et al. [27]	1993	11	Equilibrium
Maiti et al. [28]	1995	22	Anisotropy decay
Maiti et al. [29]	1998	5	Spectral narrowing
Kobayashi et al. [10]	1999	3–7	Equilibrium
Koti et al. [30]	2003	5–13	Spectral narrowing
Misawa and Kobayashi [11]	1998	4–6	Polarizability change
<i>Present study</i>	2004	60–80	<i>Polarizability change</i>
<i>Cyanine (PIC)</i>			
Misawa and Kobayashi [8]	1995	80–120	Polarizability change
<i>Cyanine (DiSC)</i>			
Chowdhury et al. [12]	1995	4–6	Polarizability change

$$F = \left(\frac{\varepsilon + 2}{3}\right) \frac{F_{\text{ext}}}{\varepsilon} = \left(\frac{1}{3} + \frac{2}{3\varepsilon}\right) F_{\text{ext}} \quad (7)$$

with a macroscopic field of $F_{\text{ext}}/\varepsilon$ and the dielectric constant ε of 5.9 in a homogeneous PVA film.

4. Results and discussion

4.1. Evaluation of stark parameters

The Stark parameters determined are shown in Table 1, where the values were evaluated within the two limits of orientational distributions: Those for monomer were evaluated from Eq. (2) (3-D isotropic) and Eq. (4) (completely oriented), while those for J-aggregate were from Eq. (3) (2-D isotropic) and Eq. (4) (completely oriented). It was difficult to correctly estimate the degree of orientation, because $|\Delta\mu|_{2f}$ estimated from the Kerr effect

gives just a maximum value for $|\Delta\mu|$. The Kerr-signals of TPPS could be fitted with the contribution of $\Delta\alpha$ alone.

Table 1 shows that $|\Delta\alpha|$ increases by a factor of ≈ 60 –80 by forming J-aggregates. The red-shifted bands of the J-aggregate have the transition moment along the alignment direction of the molecules. This finding shows that the static polarizability in the direction of the aggregation axis of porphyrin J-aggregate greatly changes by photo-excitation, as in the case of PIC J-aggregates [8]. By contrast, it is unusual that the Pockels signals were observed for the samples without poling, as was also observed for PIC J-aggregates [21]. It is difficult to determine, only from the present results, whether or not $|\Delta\mu|$ increases by forming J-aggregates. The intensity of the Pockels signal was strongly sample-dependent, ranging from near zero to the most intense signals shown in Fig. 1c and d. Originally, TPPS monomer has no permanent electric dipole moment due to the inversion symmetry of the ground electronic state. The results in Fig. 1c and d indicate that symmetry breaking takes place in the polymer matrix environment. In addition, J-aggregates are known to be highly oriented by the vertical spin coating method [8,11]. Although we adopted the conventional spin coating method, it may lead to a partial orientation in the direction of centrifugal force in the spinning process. The observed strong sample dependence is likely to arise from these reasons.

4.2. Modulation-frequency dependence

We investigated the dependence of $\Delta\mu$ and $\Delta\alpha$ on the modulation parameters, i.e., the amplitude of the applied electric field and the modulation frequency. The values of $\Delta\mu$ and $\Delta\alpha$ were independent of the electric-field amplitude around $F_0 \approx 10^6$ V/m, but for some samples the modulation frequency dependence of the absorbance change was observed for $f = 235$ –2035 Hz as shown in Fig. 2.

Since the change in absorbance is due to that in the electronic distribution in the J-aggregate, it should have no modulation-frequency dependence in this frequency range. However, some samples show an increase in absorbance change with decreasing frequency (sample g_a). This is most likely caused by reorientation of TPPS, since they are not covalently fixed in PVA, but located in a spatial vacancy in the polymer network of PVA.

Some samples show a decrease in absorbance change with frequency (sample d_a – f_a). Sometimes the same sample shows this frequency dependence when the humidity of laboratory is high, but never at low humidity. These observations can be explained by the change in the local-field behavior due to the frequency-dependent dielectric constant ε of a PVA matrix. A hydrophilic-polymer film like PVA contains moisture in highly humid environment. When many water molecules

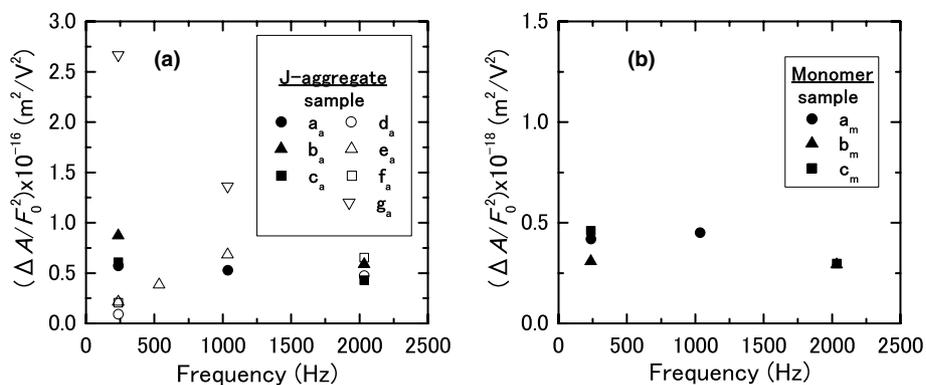


Fig. 2. Applied electric field frequency dependence of the absorbance change due to the Kerr effect for (a) seven different samples of J-aggregate probed at 2.52 eV and (b) three different samples of monomer probed at 2.91 eV.

enter into main polymer chains, interaction between chains is reduced and its dielectric constant ϵ increases with decreasing frequency from 10^5 to 10^2 Hz [22]. The frequency dependence of ϵ for moistened PVA film was actually detected in this frequency range [23].

Eq. (7) shows that local-field $|\vec{F}|$ decreases when the dielectric constant ϵ increases. For instance, a change in the modulation frequency f from 2035 to 235 Hz causes a decrease in the local-field $|\vec{F}|$ and the resultant reduction in the absorbance change. If this is the case, then the dielectric constant ϵ cannot be fixed at 5.9 to determine $\Delta\mu$ and $\Delta\alpha$.

In order to avoid these extra effects, the Stark parameters in Table 1 are obtained for samples without modulation-frequency dependence, three pairs of TPPS J-aggregate and monomer sample of a_a – c_a and a_m – c_m in Fig. 2. Note also that the signal intensity tends to converge as the modulation frequency is increased and that stable Stark parameters could be obtained above $f = 2000$ Hz.

4.3. Scaling laws

For 1-D π -conjugated systems, nonlinear polarizability has been shown to have scaling laws in terms of the coherence length [24–26]. Similarly, the increase in $\Delta\alpha$ reflects the coherence aggregation number N_c . When a simple two-level system (the ground and one-exciton states) is considered, it holds that $\Delta\alpha_{\text{agg}} = N_c \Delta\alpha_{\text{mon}}$ [8,9] and $\Delta\mu_{\text{agg}} = \Delta\mu_{\text{mon}}$ [15,31]. Here, $\Delta\alpha_{\text{agg}}$ and $\Delta\alpha_{\text{mon}}$ are the changes in the static polarizability of J-aggregate and monomer, and $\Delta\mu_{\text{agg}}$ and $\Delta\mu_{\text{mon}}$ are those in the static dipole moment. When other excited states higher than the lowest are considered, the N_c estimated from the increase in the polarizability change is expected to become larger [13,14]. In particular, it is discussed in [14] that the contribution of the two-exciton state to $\Delta\alpha$ should nearly cancel the increase in $\Delta\alpha$ for J-aggregate. However, this model would not be able to account for the substantial increase in $\Delta\alpha$ observed in the exper-

iments, which requires more sophisticated experimental and theoretical tests. The N_c for TPPS can be estimated from the scaling law for $\Delta\alpha$ to be 60–80.

The N_c s of J-aggregate have so far been estimated for several dye species using the scaling law [11,8,12]; smaller value than the present estimate is reported in [11] despite the similarity in the experimental conditions. This discrepancy is possibly due to the frequency dependence of the dielectric constant, since the value in [11] is within the range of our observation in Fig. 2. In [11], the same hydrophilic polymer of PVA was used as a matrix material, and the lower modulation frequency of 300 Hz was employed. Therefore the absorbance change due to the Stark effect would have been substantially influenced by the moisture contained in PVA film.

The N_c of 60–80 is larger than that previously reported for TPPS, as listed in Table 2 [27–30] but it is on the same order of the N_c of cyanine J-aggregate, which was estimated to be 100 ± 20 [8]. Moreover, the present value is the aggregation number in polymer, while the results in [27–30] are those in water. It is possible for the coherence length to be larger in the presence of polymer. That is, the J-aggregate coherence length in macro-aggregates may depend sensitively on environment.

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